



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

0 167 375  
A2

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 85304672.0

(51) Int. Cl.4: C 11 D 3/39

(22) Date of filing: 01.07.85

(30) Priority: 02.07.84 US 626825

(71) Applicant: The Clorox Company  
1221 Broadway  
Oakland California 94612(US)

(43) Date of publication of application:  
08.01.86 Bulletin 86/2

(72) Inventor: Hsieh, Chung Lu  
35 St Pierre Court  
San Ramon California 94583(US)

(84) Designated Contracting States:  
BE CH DE FR GB IT LI LU NL SE

(72) Inventor: Kong, Stephen Bradford  
3318 Washington Court  
Alameda California 94501(US)

(54) Stable bleaching compositions.

(72) Inventor: Steichen, Dale Stanley  
5734 Haggin Oaks Avenue  
Livermore California 94550(US)

(57) This invention provides stable peroxyacid bleaching compositions comprising:

(72) Inventor: Wheeler, Harold Randolph  
1362 Calais Avenue  
Livermore California 94550(US)

(a) a surface active peroxyacid, and  
(b) at least one surfactant which forms a mixed micelle in aqueous solution with said peroxyacid;  
wherein said aqueous solution contains a detergent concentration of about 0.1 to 3.0 grams/liter.

Buffers and other typical cleaning adjuncts known to those skilled in the art may be included.

The invention also provides a method of stabilizing the decomposition rate of surface active peroxyacids.

(74) Representative: Ford, Michael Frederick et al.  
MEWBURN ELLIS & CO. 2/3 Cursitor Street  
London EC4A 1BQ(GB)

BEST AVAILABLE COPY

EP 0 167 375 A2

STABLE BLEACHING COMPOSITIONS

This invention relates to surface active peroxyacids useful for bleaching and means of substantially decreasing their decomposition in aqueous solution.

Although some surface active bleaching compositions 5 have been introduced for various applications, stability problems and other attendant difficulties have prevented their widespread use.

It has been surprisingly discovered that the decomposition of certain surface active peroxyacids can be 10 stabilised or affected by the addition of certain surfactants. By addition of these surfactants, second order decomposition rates of the selected peroxyacids in aqueous medium can be significantly reduced. As a result, greatly increased amounts of available oxygen of these peroxyacids 15 is present for use.

In one embodiment of this invention is provided a stable peroxyacid bleach composition comprising:

(a) a surface active peroxyacid, and  
(b) at least one surfactant which forms a mixed 20 micelle in aqueous solution with said peroxyacid;

wherein said aqueous solution contains a detergent concentration of about 0.1 to 3.0 grams/liter.

In yet another embodiment of the invention, is provided a stable peroxyacid bleach composition comprising:

a) a surface active, peroxyacid having a carbon chain of from 6 to 20 carbon atoms;

5 (b) at least one surfactant which forms a mixed micelle in aqueous solution with said peroxyacid; and

(c) a buffer to keep the composition within the range of pH 7-12 when in aqueous solution with detergent;  
wherein said aqueous solution contains a detergent  
10 concentration of about 0.1 to 3.0 grams/liter.

This invention also includes a method for stabilising the decomposition rate of peroxyacids comprising;

(a) combining a surface active peroxyacid with at least one surfactant; and

15 (b) forming a mixed micelle in aqueous solution therebetween  
wherein said aqueous solution contains a detergent  
concentration of about 0.1 to 3.0 grams/liter.

Further, is provided a method for bleaching soiled fabrics comprising:

20 treating a soiled fabric with a composition which comprises

(a) a surface active peroxyacid;

(b) at least one surfactant which forms a mixed micelle in aqueous solution with said peroxyacid; and

removing the soil from said soiled fabric;

5. wherein said aqueous solution contains a detergent concentration of about 0.1 to 3.0 grams/liter.

The applicants have discovered that under certain conditions, the dispersion of various surface active peroxyacids in aqueous 10 solution will lead to unexpectedly swift decomposition, leading to loss of available oxygen. This heretofore unrecognized problem has been solved by the present invention which stabilizes these decomposition rates by the addition of particular surfactants. Many different examples of these peroxyacids were inspected at 15 various pH's and temperatures. In certain cases, especially with regard to the alkyl diperoxysuccinic acid decompositions, it was noted that at temperatures lower than that for the typical warm water wash ( $70^{\circ}\text{F}$  or  $21.1^{\circ}\text{C}$ ) that the decomposition rate was even swifter than at higher temperatures. This led to the 20 proposal that the particular peroxyacids studied may form micelles in aqueous solution. These micelles have the effect of localizing the peroxyacid head groups (i.e., the peroxy moieties,  $\text{C}-\text{O}-\text{O}-\text{OH}$ ).

25 It is speculated that the presence of these exposed peroxy groups in close proximity to each other increases the decomposition rate. The foregoing theory is believed to be

ascertained by the experiments in the EXPERIMENTAL section which follows, however, the applicants herein do not intend to be bound thereby, as the complex reaction kinetics of these particular systems may give rise to yet other plausible theories which at 5 present have not yet been discovered.

Just as significantly, at certain pH's, the surface active peroxyacids are particularly effective. These pH's correspond to the  $pK_a$ 's of such surface active peroxyacids. According to 10 theory, which applicants again advance, but by which they do not wish to be bound, peroxyacid moieties in aqueous solution dissociate as follows:



15 wherein K is the equilibrium constant.

and, accordingly, when 50% of dissociation is reached, is measured as the  $pK_a$ . Optimal performance is believed to be reached at pH's close to the  $pK_a$ . For certain surface active peroxyacids, 20 such  $pK_a$ 's are believed to be in range of pH 8.5 - 9.5. Simultaneously, the normal pH found in American laundry machines is around pH 8-10. As previously mentioned, optimal activity, hence optimal bleaching, may occur at pH 8.5 - 9.5. However, it is within this critical range that increased decomposition of the surface active peroxyacids was noted. The problem faced was how 25 to preserve an effective amount of peroxyacid at these pH's.

Thus, in aqueous solution, organic peroxyacids are not noted for their stability and may lose available oxygen. Further, although previously unknown in the art, it has recently been

discovered that certain peroxyacids, particularly surface active alkyl peroxyacids may undergo extremely rapid solution decomposition when they are dispersed in water. While the solution kinetics of alkyl peroxyacids in aqueous solution are complex and not completely understood, it is believed that such surface active alkyl peroxyacids form micelles wherein the reactive head groups are oriented to the exterior of such micelles and, may be caused to decompose more rapidly due to a localized high peroxyacid concentration. This in turn is believed to enhance intermolecular decomposition. These particular problems have never been previously recognized in the art.

Many references have shown the combination of a peroxyacid with a surfactant (see for example, U.S.4,374,035, issued to Bossu). Surfactants are normally present as either the normal constituents of a laundry detergent or bleaching product, or, as in the case of U.S.4,374,035, as a formulation ingredient to delay the release of the active bleaching species. However, there has been no recognition in the art that such surfactants prevent the rapid decomposition of surface active peroxyacids in aqueous solution.

20

Surprisingly, the addition of a surfactant capable of forming a mixed micelle with said peroxyacids in aqueous solution has been found to stabilize these peroxyacids. By mixed micelles, it is to be understood that when two surface active molecules are combined, they may form micelles together. The mixed micelles are believed to be present if stability, i.e., loss of available oxygen is controlled or diminished. This can be observed if half-life of the peroxyacid is increased. Further, addition of the surfactants appears to decrease the decomposition rate and thus improves the

amount of available oxygen for enhanced bleaching performance. It is believed that the use of these surfactants in principle forms mixed micelles with the peroxyacids resulting in the decrease of intermolecular interactions among peroxy acid molecules and thus decreases the decay rates. The result of stabilizing these peroxyacids is that higher active concentrations of a peroxyacids remain when they are in a wash water solution. This has the salutary benefit of greatly increasing the performance of these peroxyacids on stained fabrics as opposed to non-stabilized peroxyacids in aqueous solution.

10

The many types of each individual component of these stable peroxyacid bleach compositions of this invention are described as follows:

15 1. Peroxyacids:

Suitable surface active peroxyacids include those monoperoxyacids having from 6 to 20 carbon atoms in the carbon chain. Suitable monoperoxyacids include for example perhexanoic, peroctanoic, pernonanoic, perdecanoic, and perdodecanoic (perlauric) acids.

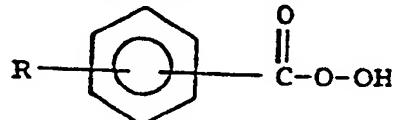
20 Examples of further suitable peroxyacids are the alpha substituted alkyl monoperoxy and diperoxyacids, such as alkyl diperoxy succinic acid, shown in Published European Patent Application 0083 056, whose disclosure is incorporated herein by reference. A representative example of an alpha or beta substituted monoperoxyacid is  $\alpha$  or  $\beta$  alkyl monoperoxy succinic acid containing 6-20 carbon chains in the alkyl group which is the subject of our pending US Patent Application No 626826,

11/14 July 75  
0167375

- 7 -

and corresponding European application no . . . . .  
claiming priority therefrom, which is entitled "Alkyl  
Monoperoxy succinic Acid Bleaching compositions and  
Synthesis and Use Thereof" whose disclosure is incorpora-  
5 ted herein by reference.

Yet other examples of the preferred peroxyacids  
used herein include substituted or unsubstituted aryl-  
peroxyacids with an alkyl group of 6 to 20 carbon  
atoms. An Example thereof is the peroxyacid having  
10 the following structure:



wherein R is a carbon chain comprising  
6 to 20 carbon atoms.

15 Mixtures of the above peroxyacids may also be useful  
in the inventive composition.

The common property possessed by all the foregoing examples of  
preferred peroxyacids appears to be that all must be surface  
active. Those surface active peroxyacids may also be classified  
as hydrophobic bleaches. A "hydrophobic" bleach has been defined  
20 in Published European Patent Application 0 068.547 (the disclosure  
of which is incorporated herein by reference) as "one whose parent  
carboxylic acid has a measurable CMC (critical micelle  
concentration) of less than 0.5M." This definition assumes that  
the CMC will be measured in aqueous solution at 20°C-50°C. As  
will be more explicitly discussed in the ensuing description, it  
25 appears essential that the peroxyacids of this invention form  
micelles in aqueous solution. It is this particular phenomenon  
which causes the heretofore unknown rapid decomposition rates of  
the peroxyacids. This rapid decomposition is remedied by the  
addition of the surfactants disclosed in this invention.

2. Surfactants:

Suitable surfactants for use in stabilizing the peroxyacids of this composition are selected from anionic, nonionic, amphoteric, and zwitterionic surfactants and mixtures thereof. Various 5 anionic, nonionic, amphoteric, and zwitterionic surfactants and mixtures thereof appear to significantly affect the decomposition rates of the peroxyacids of this invention.

Anionic surfactants suitable for use in this invention 10 generally include fatty acids, their alkali metal and ammonium salts and their ethoxylated homologs having about 8-20 carbon atoms in their alkyl chain lengths; substituted and unsubstituted alkyl sulfonates; substituted and unsubstituted alkyl benzene sulfonates (examples of which include both "HLAS", for alkylbenzene sulfonic acid, and "LAS", for linear alkyl benzene 15 sulfonate, sodium salt). Still other suitable anionic surfactants include anionic aminocarboxylates, such as N-acyl-sarcosinates, alkyl, aryl, and alkyaryl sarcosinates; alpha-olefin sulfonates; sulfates of natural fats and oils (e.g., castor, coconut, tallow oils); sulfated esters; ethoxylated and sulfated alkylphenols; 20 ethoxylated and sulfated alcohols (also known as alkyl ether sulfates) and phosphated esters which are generally phosphorylated nonionics such as ethoxylated alcohols, ethoxylated alkylphenols, and polyoxyethylene-polyoxypropylene block co-polymers.

25 It has been found that particularly preferred anionic surfactants used in this invention are fatty acids and their alkali metal salts having at least 8 carbon atoms in their alkyl group. Of these, particularly preferred are the potassium salts,

such as potassium palmitate, myristate, and stearate. It is not exactly understood why these particular surfactants may be preferred for use, however the potassium cation is generally known in the art to be more soluble than other alkali metal salts, such as sodium. Further, it is possible that the carboxylate group in these surfactants are the reason for the compatibility between surfactant and peroxyacid molecules. It is also believed that increased stability may occur when these surfactants' alkyl chain groups are about the same length or slightly longer (i.e., at least one carbon more) than those of the peroxyacid. It is speculated that with proper alkyl chain length presence (i.e., a surfactant able to form a mixed micelle), the resulting energetically favorable mixed micelle formation contributes to the stability of the peroxyacid molecules. (see below, TABLES I-III).

Suitable nonionic surfactants may include linear and branched ethoxylated alcohols; linear and branched propoxylated alcohols; ethoxylated and propoxylated alcohols; polyoxyethylenes, alkyl polyoxypropylenes; alkylpolyoxyethylenes; alkylarylpolyoxyethylenes; ethoxylated alkylphenols; carboxylic acid esters such as glycerol esters of fatty acids, certain polyethylene glycol esters, anhydrosorbitol esters, ethoxylated anhydrosorbital esters, ethylene and methylene glycol esters, propanediol esters, and ethoxylated natural fats and oils (e.g., tallow oils, coco oils, etc.); carboxylic amides such as 1:1 amine acid diethanolamine condensates, 2:1 amine/acid diethanolamine condensates, and monoalkanolamine condensates such as ethanolamine condensates, and isopropanol-amine condensates, polyoxyethylene fatty acid amides; certain polyalkylene oxide block co-polymers such as polyoxypropylene-polyoxyethylene block co-polymers; and other miscellaneous nonionic surfactants such as organosilicones.

Cationic surfactants may also be suitable for inclusion in the invention. Cationic surfactants include a wide range of classes of compounds, including non-oxygen-containing alkyl mono-, di and polyamines, and resin derived amines; oxygen-containing amines, such as amine oxides (which appear to act as cationics in acidic 5 solutions, and as nonionics in neutral or alkaline solutions); polyoxyethylene alkyl and alicyclic amines; substituted alkyl, alkylol imidazolines, such as 2-alkyl-1-(hydroxyethyl)-2-imidazolines; amide linked amines, and quaternary ammonium salts ("quats"):

10

Further, suitable amphoteric surfactants containing both acidic and basic hydrophilic moieties in their structure, include alkyl betaines, amino-carboxylic acids and salts thereof, amino-carboxylic acid esters, and others.

15

Further examples of anionic, nonionic, cationic and amphoteric surfactants which may be suitable for use in this invention are depicted in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, Vol. 22, pages 347-387, and McCutcheon's Detergents 20 and Emulsifiers, North American Edition, 1983, incorporated herein by reference.

20

Zwitterionic surfactants which may be suitable for use in the compositions of this invention may be broadly described as 25 derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium

compounds. Suitable examples of these zwitterionic surfactants can be found described in Jones, US 4,005,029, Columns 11-15, which are incorporated herein by reference.

5 Preferred ranges of the compositions of this invention comprising the above described peroxyacids and surfactants are as follows:

10 Peroxyacid: 1-100 ppm A.O., more preferably 1-50 ppm A.O., most preferably 1-25 ppm A.O. when in aqueous solution. (A.O stands for active oxygen).

Surfactants: 1-10,000 ppm, more preferably 1-5,000 ppm, most preferably 1-1,000 ppm when in aqueous solution.

15 In order to deliver these amounts, it is preferred that a dry product contain about 0.1 to 20.0% by weight of the peroxyacid and about .01 to 80.0% by weight of the surfactant, the remainder comprising filler.

20 In yet a further embodiment of this invention, a buffer is present. These buffers may be selected from the alkali metal, ammonium and alkaline earth metal salts of borates, nitrates, iodates, hydroxides, carbonates, silicates or phosphates. Organic buffers such as TRIS, salts of tartaric, oxalic, phthalic, 25 benzoic, succinic, citric, and maleic acids may also be suitable for use herein. The presence of these buffers may be useful in

establishing desired pH ranges in the wash water or other aqueous system. Mixtures of these buffers may also be suitable. For the purposes of this invention, it appears that a pH range of 7-12 may be preferable. Differences in temperature may also affect the performances of the peroxyacids in this invention. For example, 5 it was commonly assumed that higher temperatures may promote more rapid decomposition of the peroxyacids herein. However, with particular regard to alpha-substituted alkyl diperoxysuccinic acid, it was found that there was greater instability at 25°C than at 37.8°C and 54.5°C. Also, further adjuncts known to 10 those skilled in the art may be included in these compositions.

#### EXPERIMENTAL

TABLES I-III below show the half-life values obtained for 15 particular peroxyacids which were stabilized with surfactants. The surfactants used here included: sodium linear alkyl benzene sulfonate, fatty acids, and sodium alkyl sulfate; other anionic surfactants such as alkali metal salts of fatty acids (potassium myristate, potassium palmitate); and nonionic surfactants, such as 20 Triton X-114 (trademark of Rohm & Haas for octylphenoxy poly- (ethyleneoxy)ethanol) and Neodol 25-9 (trademark of Shell Chemical Company for linear ethoxylated alcohol with a predominant chain of 12-15 carbons and averaging 9 moles of ethylene oxide per mole of alcohol). Adjusting for use with buffer, all peroxyacids tested 25 showed marked improvements in their half-lives when the surfactants were added.

Additionally, the preferred fatty acid salts provided especially increased stabilization for the peroxyacids surveyed. (See TABLE I, Examples 4,7; TABLE II, Example 19-22, 24-25).

5 The stable bleaching compositions of the invention could be put to commercial use as a stable dry bleach product. For example, the conditions under which these stable bleaching compositions were tested used "real-life" washing conditions, wherein commercial detergents, e.g., Tide® (Procter & Gamble Co.) and Fresh Start® (Colgate-Palmolive Co.) were added to 10 wash water in amounts which follow prescribed usage. For the purposes of this invention, this is about 0.1 to 3.0 grams/liter, based on the dry weight of the detergent, with about 0.5 to 1.60 grams/liter normally the average usage.

15 The invention is further exemplified by the experimental data set forth below and by the claims hereto, although the applicants do not thereby intend to restrict the scope of their invention.

0167375

TABLE I  
PERDECANOIC AND PERDODECANOIC ACID HALF-LIFE  
STABILIZATION BY SELECTED SURFACTANTS

<u>Example</u>	<u>Peroxyacid</u>	<u>Detergent</u>	<u>Temperature</u>	<u>Buffer</u>	<u>pH</u>	<u>Surfactant</u>	<u>Half-Life (Seconds)</u>
1	Perdecanoic Acid <sup>1</sup>	Tide® 2	21.1°C	0.1M <sup>3</sup>	9	None	1,500
2	"	"	"	"	"	Lauric <sup>4</sup> Acid	1,600
3	"	"	"	"	"	Palmitic <sup>5</sup> Acid	3,750
4	"	"	"	"	"	Potassium <sup>6</sup> Myristate	13,000
<u>Example</u>	<u>Peroxyacid</u>	<u>Detergent</u>	<u>Temperature</u>	<u>Buffer</u>	<u>pH</u>	<u>Surfactant</u>	<u>Half-Life (Seconds)</u>
5	Perdodecanoic <sup>1</sup> Acid	Tide® 2	21.1°C	0.1M <sup>3</sup>	9	None	260
6	"	"	"	"	"	Lauric <sup>4</sup> Acid	3,500
7	"	"	"	"	"	Potassium <sup>6</sup> Myristate	8,000

1 Concentration was  $1.25 \times 10^{-3}$ M or 20 ppm A.O.

2 Tide® is a registered trademark of Procter & Gamble Co. 1.53 g/l were used.

3 Buffer was 0.1M Na<sub>2</sub>CO<sub>3</sub>.

4 Lauric acid is a C12 fatty acid, which, at this pH, forms a salt. About  $2.5 \times 10^{-3} M$  was present.

5 Palmitic acid is a C16 fatty acid, which, at this pH, forms a salt. About  $2.5 \times 10^{-3} M$  was present.

6 Potassium myristate is a C14 fatty acid monopotassium salt. About  $2.5 \times 10^{-3} M$  was present.

0167375

TABLE II  
ALKYL DIPEROXY SUCCINIC ACIDS  
STABILIZATION BY SELECTED SURFACTANTS

<u>Example</u>	<u>Peroxyacid</u>	<u>Detergent</u>	<u>Temperature</u>	<u>Hardness</u>	<u>pH</u>	<u>Surfactant</u>	<u>Half-life (seconds)</u>
8	Dodecyl Diperoxy1, Tide® 2 Succinic Acid		37.80C	100ppm <sup>3</sup>	8.5	None	120
9				"	"	Niaproof <sup>4</sup>	90
10				"	"	Polystep B-265	120
11				"	"	C <sub>12</sub> Alkyl Sulfate	180
12				"	"	Sodium Laurate	180
13				"	"	Calsoft F-906	185
14				"	"	Triton X-457	270
15				"	"	Alfonic 1412-408	300

16	"	"	"	"	Triton X-114 <sup>9</sup>	330
17	"	"	"	"	Alfonic 1618-6510	390
18	"	"	"	"	Neodol 25-911	450
19	"	"	"	"	Potassium Stearate <sup>12</sup>	600
20	"	"	"	"	Potassium Palmitate <sup>13</sup>	790
21	"	"	"	"	Sodium Myristate <sup>14</sup>	900
22	"	"	"	"	Potassium Myristate <sup>15</sup>	1080
23	Decyl Diperoxy <sup>1</sup> Succinic Acid	Tide <sup>②</sup> 2	37.80C	100ppm <sup>3</sup>	8.5	None
24	"	"	"	"	Potassium Palmitate <sup>13</sup>	240
25	"	"	"	"	Potassium Palmitate <sup>13</sup>	600

1 Concentration was  $6.25 \times 10^{-4}M$  or 20 ppm A.O.

2 Tide<sup>②</sup> is a trademark of the Procter & Gamble Company. 1.53 g/liter were used.

3 Hardness: measured as  $\text{CaCO}_3$ .

4 Trademark of Niaset Chemicals for  $\text{C}_{14}$  alkyl sulfate. Each of the following surfactants was present at about 1.41 g/ 3 liters solution (100% activity), or about 470 ppm.

0167375

0167375

- 18 -

- 5 Trademark of Stepan Chemicals for C<sub>16</sub>-18 alkyl sulfate.
- 6 Trademark of Pilot Chemical Co. for C<sub>11</sub>.3 alkyl benzene sulfonate.
- 7 Trademark of Rohm and Haas for octylphenol -4- ethoxylate.
- 8 Trademark of Conoco Chemical Co. for C<sub>12</sub>-14 alcohol ethoxylate sulfate.
- 9 Trademark of Rohm and Haas for octylphenol -8- ethoxylate.
- 10 Trademark of Conoco Chemical Co. for C<sub>16</sub>-18 alcohol -8- ethoxylate.
- 11 Trademark of Shell Chemical Co. for C<sub>12</sub>-15 alcohol -9- ethoxylate.
- 12 C<sub>18</sub> fatty acid monopotassium salt.
- 13 C<sub>16</sub> fatty acid monopotassium salt.
- 14 C<sub>14</sub> fatty acid monosodium salt.
- 15 C<sub>14</sub> fatty acid monopotassium salt.

- 19 -

TABLE III  
PERDECANOIC ACID HALF LIFE  
STABILIZATION BY SELECTED SURFACTANTS

<u>Example</u>	<u>Peroxyacid</u>	<u>Detergent</u>	<u>Temperature</u>	<u>Buffer</u>	<u>pH</u>	<u>Surfactant</u>	<u>Half-Life(Seconds)</u>
26	Perdecanoic1	Fresh Start2	21.10C	0.1M3	9	None	4,300
27	"	"	"	"	"	Neodol 25-74	5,100
28	"	"	"	"	"	Sodium Lauryl5 Sulfate	5,500
29	"	"	"	"	"	Myristic Acid6	9,000

1 Concentration was  $1.25 \times 10^{-3} M$  or 20 ppm A.O..2 Fresh Start is a trademark of Colgate-Palmolive Co. For detergent containing nonionic surfactant.  
Present at 0.5g / liter.3 Buffer was  $Na_2CO_3$  at 0.1M.4 Trademark of Shell Chemical Co. for linear alcohol ethoxylate with a predominant chain length of 12-15 carbons,  
and averaging 7 moles of ethylene oxide per mole of alcohol. Present at about  $2.5 \times 10^{-3} M$ .5 Sodium dodecyl sulfate, anionic surfactant. Present at about  $2.5 \times 10^{-3} M$ .6 Myristic acid at this pH forms fatty acid salt. Present at about  $2.5 \times 10^{-3} M$ .

## CLAIMS:

1. A stable peroxyacid bleach composition comprising:
  - (a) a surface active peroxyacid; and
  - (b) at least one surfactant which forms a mixed micelle in aqueous solution with said peroxyacid;

5 wherein said aqueous solution contains a detergent concentration of about 0.1 to 3.0 grams/liter.
2. The stable peroxyacid bleach composition of claim 1 wherein said peroxyacid comprises about 0.1 to 20.0% by weight and said surfactant comprises .01 to 80.0% by weight.
- 10 3. The stable peroxyacid bleach composition of claim 1 or claim 2 further comprising a buffer.
4. The stable peroxyacid bleach of claim 3 wherein said buffer is selected from the alkali metal, ammonium, and alkaline earth salts of borates, nitrates, iodates, hydroxides, carbonates, silicates, and phosphates; organic buffers; and mixtures thereof.
- 15 5. The stable peroxyacid bleach composition of any one of the preceding claims wherein the peroxyacid has a carbon chain of from about 6 to 20 carbon atoms.
- 20 6. A stable peroxyacid bleach composition comprising:
  - (a) a surface active peroxyacid having a carbon chain of from about 6 to 20 carbon atoms;
  - (b) at least one surfactant which forms a mixed

25 micelle in aqueous solution with said peroxyacid; and

(c) a buffer to keep the composition within the range of pH 7-12 when in aqueous solution with detergent; wherein said aqueous solution contains a detergent concentration of about 0.1 to 3.0 grams/liter.

5 7. The stable peroxyacid bleach composition of any one of the preceding claims wherein said surfactant is selected from anionic, nonionic, amphoteric, zwitterionic surfactants, and mixtures thereof.

8. The stable peroxyacid bleach composition of  
10 any one of the preceding claims wherein said peroxyacid is selected from:

alpha substituted alkyl diperoxysuccinic acids and alpha or beta monoperoxy succinic acids of about 6 to 20 carbon atoms in the alkyl group; straight chain  
15 monoperoxyacids of about 6 to 20 carbon atoms in the carbon chain; substituted or unsubstituted arylperoxy acids with an alkyl group of about 6 to 20 carbon atoms; and mixtures thereof.

9. The stable peroxyacid bleach composition of  
20 any one of the preceding claims wherein said surfactant is selected from alkyl fatty acids, their alkali metal salts and mixtures thereof.

10. The stable peroxyacid bleach composition of  
claim 9 wherein said surfactant has an alkyl chain containing  
25 a number of carbons approximately greater than or equal to the peroxyacid's carbon chain.

11. The stable peroxyacid bleach composition of  
claim 10 wherein said surfactant is selected from lauric,  
myristic, palmitic and stearic acid, their alkali metal  
salts and mixtures thereof.

5 12. The stable peroxyacid bleach composition of  
claim 11 wherein said surfactant is a said alkali metal  
salt which is potassium.

13. A method for reducing the decomposition rate  
of peroxyacids comprising:

10 (a) combining a surface active peroxyacid with  
at least one surfactant; and  
(b) forming a mixed micelle therebetween in aqueous  
solution;

15 wherein said aqueous solution contains a detergent  
concentration of about 0.1 to 3.0 grams/liter.

14. A method according to claim 13 wherein the peroxyacid  
and surfactant(s) are combined into a composition which  
is as defined in any one of claims 2 to 12.

15. A method for bleaching soiled fabrics comprising:  
20 treating a soiled fabric with an aqueous solution  
of a composition according to any one of claims 1 to  
12, and removing the soil from said soiled fabric; wherein  
said aqueous solution contains a detergent concentration  
of about 0.1 to 3.0 grams/liter.

**THIS PAGE BLANK (USPTO)**



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

⑯ Publication number:

**0 167 375**  
**A3**

⑯

## EUROPEAN PATENT APPLICATION

㉑ Application number: 85304672.0

㉑ Int. Cl. 1: **C 11 D 3/39**

㉒ Date of filing: **01.07.85**

㉓ Priority: **02.07.84 US 626825**

㉑ Applicant: **The Clorox Company, 1221 Broadway, Oakland California 94612 (US)**

㉔ Date of publication of application: **08.01.86**  
**Bulletin 86/2**

㉒ Inventor: **Hsieh, Chung Lu, 35 St Pierre Court, San Ramon California 94583 (US)**  
**Inventor: Kong, Stephen Bradford, 3318 Washington Court, Alameda California 94501 (US)**  
**Inventor: Stelchen, Dale Stanley, 5734 Haggin Oaks Avenue, Livermore California 94550 (US)**  
**Inventor: Wheeler, Harold Randolph, 1362 Calais Avenue, Livermore California 94550 (US)**

㉕ Designated Contracting States: **BE CH DE FR GB IT LI LU NL SE**

㉔ Representative: **Smith, Sydney et al, Elkington and Fife High Holborn House 52/54 High Holborn, London WC1V 6SH (GB)**

㉖ **Stable bleaching compositions.**

㉗ This invention provides stable peroxyacid bleaching compositions comprising:

(a) a surface active peroxyacid, and  
(b) at least one surfactant which forms a mixed micelle in aqueous solution with said peroxyacid;  
wherein said aqueous solution contains a detergent concentration of about 0.1 to 3.0 grams/liter.

Buffers and other typical cleaning adjuncts known to those skilled in the art may be included.

The invention also provides a method of stabilizing the decomposition rate of surface active peroxyacids.

**EP 0 167 375 A3**



European Patent  
Office

EUROPEAN SEARCH REPORT

0167375  
Application number

EP 85 30 4672

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-4 455 252 (K.B. WYLEGALA et al.) * Examples; claims *	1, 9	C 11 D 3/39
A	--- US-A-3 956 159 (J.P. JONES) * Claims *	1, 3	
A	--- US-A-4 166 794 (S. GREY) * Column 3, line 67 - column 4, line 8; claims *	1	
A	--- US-A-4 430 236 (T.Ch. FRAKS) * Claims *	1	
E	--- EP-A-0 160 342 (UNILEVER) * Claims *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
	-----		C 11 D C 07 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 20-03-1987	Examiner GOLLER P.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)